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IMPREGNATED ACTIVATED CARBON FOR DEODORANT  
[Talchuiyong Chumchak Hwalsungtan]

Sung Ho Hong, et al.

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INVENTORS	(72) :	Sung Ho Hong, et al.
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## Abstract

/1\*

The present invention deals with impregnated activated carbon that can adsorb and destroy odorants such as alkyl mercaptans and THT (tetrahydrothiophene) contained in natural gas by simple physical adsorption and chemical adsorption, wherein one or at least two substances from the group comprising KI,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_2$ ,  $\text{CoCl}_2$ ,  $\text{PdCl}_2$ ,  $\text{NaOH}$  and  $\text{CaCl}_2$  are deposited on active surface of activated carbon obtained by incomplete combustion of hydrocarbons based on impregnation, so that it may have a chemical adsorption part to adsorb and destroy odorants with strong odor based on chemical reactions on its surface.

Therefore, impregnated activated carbon of the present invention can increase efficiencies for processing odorants, destroy odorants safely without any special post-treatment processes, and extend the use period by at least 4 times more than common activated carbon used for filler material in an adsorption tower.

## Representative Diagram

Figure 3

## Specification

## Brief Description of the Drawings

Figure 1 is a graph illustrating changes in adsorption rates versus time for the existing activated carbon during repeated injection of TBM.

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Figure 2 is a graph illustrating changes in adsorption rates /2  
versus time for  $\text{FeCl}_3$  impregnated activated carbon the present  
invention during repeated injection of TBM.

Figure 3 is comparison line graphs for TBM adsorption capability  
of existing activated carbon and impregnated activated carbon  
according to the present invention.

Figure 4 is a graph illustrating changes in adsorption rates  
versus time for  $\text{CuCl}_2$  impregnated activated carbon the present  
invention during repeated injection of TBM.

#### Detailed Description of the Invention

#### Objective of the Invention

Technology to Which the Invention Belongs and Available Art of the  
Field

The present invention deals with activated carbon used to adsorb  
odorants contained in natural gas and specifically with the  
impregnated activated carbon that can adsorb and destroy odorants  
such as alkyl mercaptans and THT (tetrahydrothiopene) based on simple  
physical adsorption and also chemical adsorption.

Natural gas is a clean energy source and easy to use unlike  
other energy sources. It has high efficiencies and does not contain  
impurities so it does not release polluting substances during  
combustion.

Therefore, more natural gas is used, and its scope is being  
expanded into industrial applications as well as home applications.

National consumption of natural gas was approximately 7 million tons in 1995, and anticipated rate of increase up to year 2000 is approximately 12.2% and its consumption would reach 15.4 million tons.

While natural gas has a higher flash point and is safer than the existing fuel gas, if it is leaked, it is very likely to cause safety accidents because of its colorless and odorless physical and chemical properties. To prevent such safety accidents in advance, when natural gas is supplied from the storage tank of a delivery base to a location of use, odorants including TBM (tert-butyl mercaptan) and THT (tetrahydrothiopene) with strong odor is injected into natural gas so that users may detect natural gas leak by sense of smell and take safety actions.

However, a certain quantity of an odorant leaks during its injection, and because of strong odor of such an odorant, a small leak brings about complaints from residents surrounding its delivery base. (TBM and THT can be sensed if their concentrations are 0.77 ppb and 0.09 ppb in the air, respectively.)

To prevent this aspect, the only method adopted in Korea is to release the air inside an odorant injection room after it is passed through an adsorption tower so that any odorant leak from a delivery base may be prevented. Adsorption is used to lower the airborne concentration of an odorant below its recognition limit.

Simple activated carbon has been used as the filler material of such an adsorption tower. Such activated carbon is a solid substance

obtained by incomplete combustion of hydrocarbons and has very high surface adsorption capabilities because of its tremendously large surface area. Any odorant leaked is adsorbed on the surface of activated carbon by its adsorption capabilities owing to its high surface area, and activated carbon with a certain quantity of an odorant being adsorbed on its surface is collected and disposed because it can no longer adsorb an odorant.

Such a treatment method depends solely on single physical adsorption and has a number of problems including a limited quantity of odorants that activated carbon can treat and generation of sulfurous acid gas in the process of saturated odorant disposal.

Therefore, the method used currently to remove leaked odorants is neither very inefficient nor user friendly. So there is a need to develop new materials that will replace the activated carbon that is currently used to remove odorants.

#### Technical Objective of the Invention

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Therefore, the present invention was conceived to solve the problems above, and the objective of the present invention is to avoid simple physical adsorption by activated carbon and provide an adsorption destruction agent that converts an odorant into another substance of weak odor based on chemical reactions on its active surface.

In addition, another objective of the present invention is to provide impregnated activated carbon that may be regenerated by

leaving it at a normal temperature.

To achieve the objective above, one aspect of the present invention is that one or at least two substances from the group comprising KI,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_2$ ,  $\text{CoCl}_2$ ,  $\text{PdCl}_2$ , NaOH and  $\text{CaCl}_2$  are deposited on active surface of activated carbon obtained by incomplete combustion of hydrocarbons based on impregnation, so that it may have a chemical adsorption part to adsorb and destroy odorants with strong odor based on chemical reactions on its surface. Here, the weight of said chemical adsorption part ranges 1 wt% 30 wt% based on impregnated activated carbon, and said odorants with strong odor include alkyl mercaptans and tetrahydrothiophene (THT).

Other objectives and advantages of the present invention are described below, and become evident by its examples. In addition, the objectives and advantages of the present invention may be implemented by the means described in the claims attached and their combinations.

#### Configuration and Action of the Invention

The present inventors have realized that treatment efficiencies of an odorant could be greatly promoted for adsorption of odorants contained in natural gas with activated carbon if not only simple physical adsorption but also chemical reactions on its surface were used.

Therefore, the present inventors conceived the idea to impregnate chemical substances on active surface of said activated

carbon that could adsorb odorants of alkyl mercaptans and tetrahydrothiophene with (THT) that were generally included in natural gas or convert into other substances with weak odors.

Said alkyl mercaptans with weak odors include methyl mercaptan, ethyl mercaptan, isopropyl mercaptan, butyl mercaptan, t-butyl mercaptan, and isobutyl mercaptan. It may be guessed sufficiently by the examples below that impregnated activated carbon of the present invention is not limited to adsorption and destruction of odorants.

In addition, the present inventors have come to realize from a number of experiments that there were chemical substances that could react with odorants such as said alkyl mercaptans and tetrahydrothiophene to bring about chemical adsorption and destruction including KI,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_2$ ,  $\text{CoCl}_2$ ,  $\text{PdCl}_2$ ,  $\text{NaOH}$  and  $\text{CaCl}_2$ .

Therefore, the present invention is achieved by forming chemical adsorption parts deposited based on impregnation of said substances for odorant adsorption and destruction on active surface of the solid activated carbon obtained by incomplete combustion of hydrocarbons. While said chemical adsorption part must reach a sufficient weight ratio so as to react with odorants, excessive ratios rather reduce its surface area of activated carbon to bring about the problem with lowering physical adsorption of odorants.

Therefore, said chemical adsorption part of the present invention is formed to have the weight of 1 wt% to 30 wt% based on

the weight of impregnated activated carbon. Of course, it is preferred that the weight of said chemical adsorption part ranges 5 wt% to 20 wt% based on the weight of impregnated activated carbon.

If the weight of said chemical adsorption part becomes 1 wt% or less, almost no chemical reactions take place on the surface of the impregnated activated carbon of the present invention, and only simple physical adsorption takes place. If 30 wt% is exceeded, surface area of the activated carbon is reduced so that physical adsorption stops.

In addition, while chemical substances comprising said chemical adsorption part penetrate into activated carbon by impregnation, it is the active surface, outer surface of activated carbon, that actually reacts with odorants, so the chemical adsorption part referred to by the present invention means only the part that brings about chemical reactions with odorants contained in natural gas (the part where said chemical substances are impregnated into fine pores formed on outer surface of activated carbon).

While it is preferred to select one from the group comprising KI, NiCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>3</sub>, FeCl<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, MnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>CO<sub>2</sub>, CoCl<sub>2</sub>, PdCl<sub>2</sub>, /4 NaOH and CaCl<sub>2</sub> as a chemical substance comprising said chemical adsorption part, it is also feasible to select two or more substances from said group to mix them or form multiple layers.

In addition, that the chemical substance comprising the chemical adsorption part of the present invention is not limited by those

described above would be evident based on the point that the technical idea of the present invention involves formation of an adsorption part on active surface of activated carbon that can perform chemical destruction of odorants avoiding simple physical adsorption.

In the following is described the method for preparation the impregnated activated carbon of the present invention with the configuration above.

A. First, to obtain desired deposition rates, an aqueous solution of chemical substances including KI,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_2$ ,  $\text{CoCl}_2$ ,  $\text{PdCl}_2$ ,  $\text{NaOH}$  and  $\text{CaCl}_2$  at 0.02 to 4N is prepared to have the weight ratios of 5 : 1 to 20 : 1 based on the activated carbon to be impregnated.

B. To the aqueous solution prepared is added activated carbon so that it may be immersed in an aqueous solution.

C. After a certain period is elapsed while activated carbon is immersed in an aqueous solution, the aqueous solution is separated from activated carbon.

D. The activated carbon separated from the aqueous solution is dried at  $100^\circ\text{C}$  -  $130^\circ\text{C}$  to remove moisture.

E. The impregnated activated carbon is weighed to determine its impregnation rate.

This type of preparation is called the impregnation technique, and the impregnated activated carbon prepared in this way exhibits

fast adsorption capabilities for alkyl mercaptans based on chemical adsorption so that it can lower concentrations of odorants in a short period.

In addition, it also exhibits adsorption and destruction capabilities that can convert TBM into other substances with weak odors as for TBM (t-butyl mercaptan).

In the following is described the comparison test example concerning odorant adsorption and destruction capabilities of impregnated activated carbon and common activated carbon.

#### Comparison Example 1

In test containers of a certain size (30 ml) were placed 0.30 g of common activated carbon (activated carbon without chemical adsorption part) and activated carbon impregnated with  $\text{FeCl}_3$ , individually, and their openings were covered. Here; the test container with common activated carbon was called the A container, and the test container with  $\text{FeCl}_3$  impregnated activated carbon was called the B container.

Into said A container and B container were injected 10 ml of TBM saturated gas with a syringe, and decrease in concentrations versus time was checked with a gas chromatograph.

Here, if the TBM concentration in a container dropped to a certain concentration, 10 ml of TBM saturated gas was injected, and decrease in concentrations versus time was measured.

Results of the comparison test, described above are shown in Figures 1 and 2. Here, Figure 1 illustrates changes in adsorption rates of activated carbon in the A container, while Figure 2 illustrates changes in adsorption rates of activated carbon in the B container.

As may be found from Figure 1, in case of common activated carbon, the time required to lower the concentration of 10 ml TBM saturated gas in the A container below a certain concentration greatly increased with the number of injection.

In contrast, in case of the  $\text{FeCl}_3$  impregnated activated carbon placed in the B container, the time required to lower concentrations of odorants injected increased with the number of injections though its active area had been reduced by 15% or higher due to deposition of chemical substances compared with common activated carbon.

It may be realized from the above that the  $\text{FeCl}_3$  impregnated activated carbon of the present invention involves chemical adsorption and adsorptive destruction of TBM based on such chemical adsorption in addition to simple physical adsorption.

#### Comparison Example 2

TBM saturated gas was allowed to pass through an adsorption tower at the volume flow rate of 300 ml/min, and common activated carbon and the KI impregnated activated carbon of the present invention were used as fillers of an adsorption tower to perform adsorption curve experiments.

Its results are illustrated in the Figure 3 attached, and it may be found from Figure 3 that the time taken to saturate the filler by TBM saturated gas is greatly delayed for the KI impregnated activated carbon of the present invention compared with common activated carbon. /5

In addition, in the following are described the regeneration process of the impregnated activated carbon of the present invention and adsorption capabilities of the impregnated activated carbon regenerated by this regeneration process.

In case of the impregnated activated carbon of the present invention, it is possible to regenerate the impregnated activated carbon saturated with an odorant by leaving it at a normal temperature alone. Therefore, it reduces cost required for regeneration greatly compared with common activated carbon and is also environmental friendly because toxic gases are not generated in the regeneration step.

Adsorption capabilities of the impregnated activated carbon that has been regenerated by allowing it to stand are examined referring to Figure 3.

In the test container of a certain size (30 ml) was placed 0.30 g of  $\text{CuCl}_2$  impregnated activated carbon, its opening was covered, said  $\text{CuCl}_2$  impregnated activated carbon was saturated with TBM with a syringe, and the stopper of the test container was removed. And, the  $\text{CuCl}_2$  impregnated activated carbon was allowed to stand at a normal

temperature for a certain period to regenerate it.

To study changes in adsorption capabilities of the  $\text{CuCl}_2$  impregnated activated carbon that had been regenerated, the opening of the test container with the  $\text{CuCl}_2$  impregnated activated carbon regenerated was covered again, 20 ml of TBM saturated gas was injected into the container with a syringe, and decrease in TBM concentrations was checked with a gas analyzer to study adsorption rate changes of the  $\text{CuCl}_2$  impregnated activated carbon that had been regenerated.

If TBM concentrations in the container dropped below a certain concentration, 20 ml of TBM saturated gas was injected again, and decrease in concentrations versus time was measured.

The test results are shown in Figure 4. As it is shown in Figure 4, it may be noted that adsorption rates of the  $\text{CuCl}_2$  impregnated activated carbon of the present invention that had been regenerated were not different from adsorption rates of fresh  $\text{CuCl}_2$  impregnated activated carbon.

The present invention is not limited to the Examples described above, and it may be modified and changed by a person skilled in the art belonging to the present invention within the equivalent scope of the claims listed below under the technical idea of the present invention.

## Effects of the Invention

As described in the above, the impregnated activated carbon of the present invention has far excellent efficacy greatly exceeding the existing activated carbon in terms of adsorption rates of an odorant, quantities of an odorant to adsorb, and the regeneration technique for the impregnated activated carbon that has been saturated. That is, the impregnated activated carbon of the present invention can increase efficiencies for treating odorants, safely destroy odorants without an additional post-treatment process, and extend its use period at least 4 times compared with common activated carbon, the existing adsorption tower filler.

### (57) Claims

#### Claim 1.

Impregnated activated carbon for deodorization, wherein one or at least two substances from the group comprising KI,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_2$ ,  $\text{CoCl}_2$ ,  $\text{PdCl}_2$ , NaOH and  $\text{CaCl}_2$  are deposited on active surface of activated carbon obtained by incomplete combustion of hydrocarbon based on impregnation, so that it may have a chemical adsorption part to adsorb and destroy odorants with strong odors based on chemical reactions on its surface.

#### Claim 2.

The impregnated activated carbon for deodorization recited in Claim 1, wherein weight of said chemical adsorption part ranges 1 wt% to 30 wt% based on the activated carbon impregnated.

Claim 3.

The impregnated activated carbon for deodorization recited in /6  
Claim 1, wherein said odorants with strong odors are alkyl mercaptans  
and tetrahydrothiophene (THT).

Drawings

Figure 1

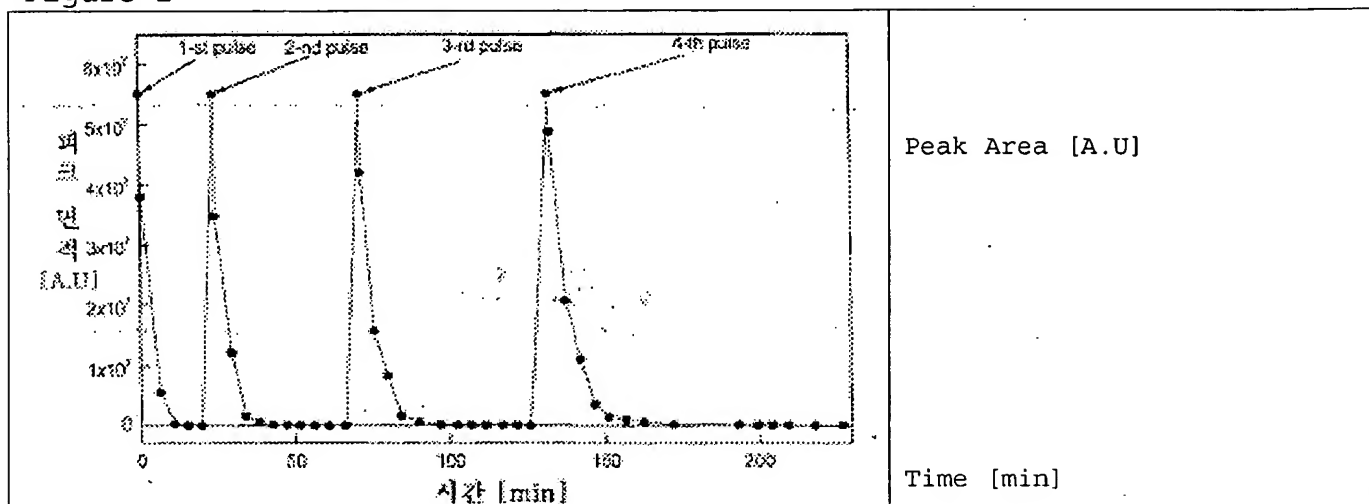


Figure 2

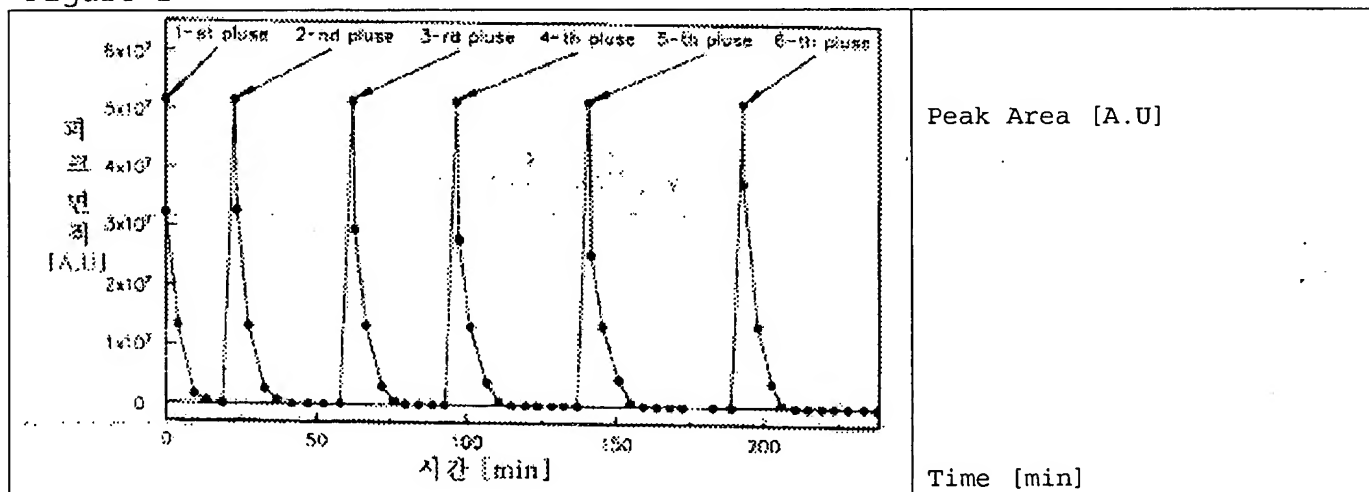


Figure 3

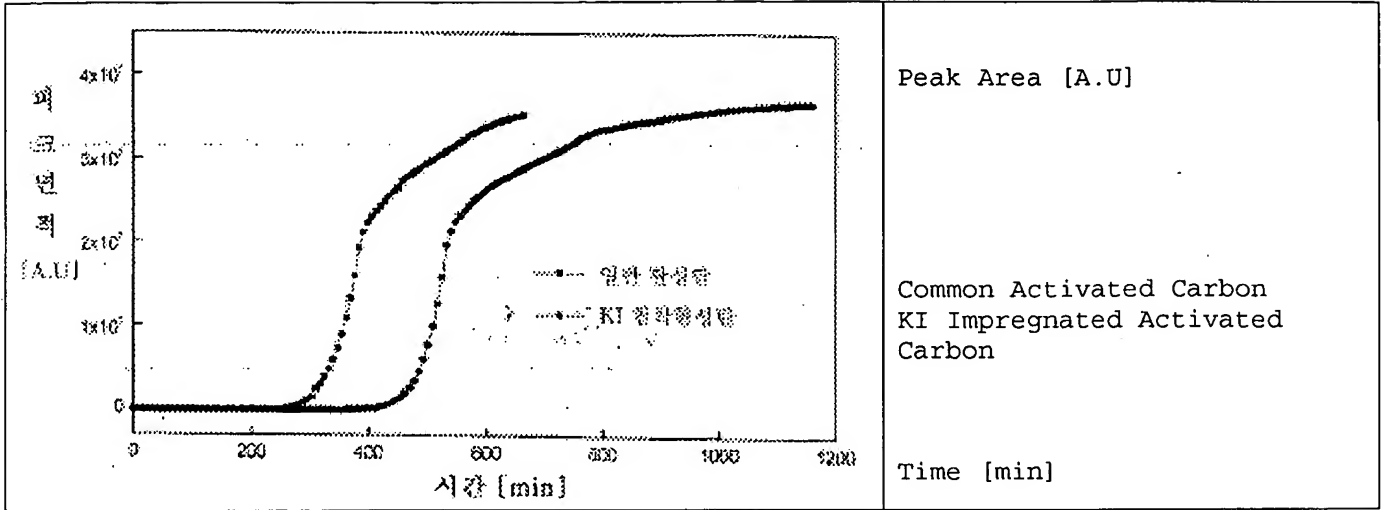


Figure 4

